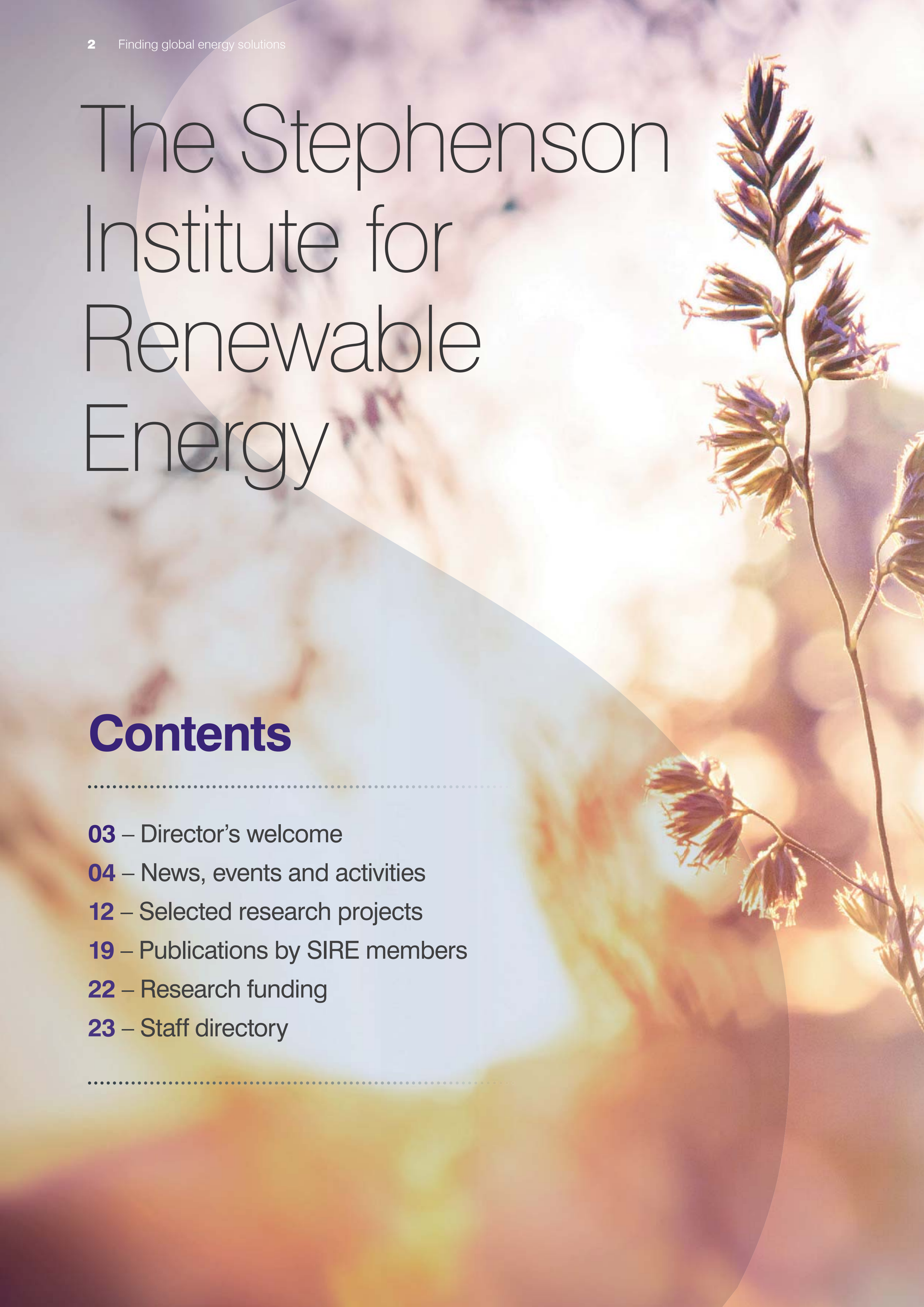
UNIVERSITY OF
LIVERPOOL

Stephenson Institute for
Renewable Energy

Stephenson Institute

Annual Report 2016

LIFE CHANGING
World Shaping



The Stephenson Institute for Renewable Energy

Contents

Director’s welcome

Welcome to the Stephenson Institute for Renewable Energy (SIRE) Annual Report for 2016 – a snapshot of our work on the physics and chemistry of energy conversion, efficiency, storage and sustainability.

Our aim is to work on topics that transform energy futures through fundamental understanding, new materials, devices and processes and our unique focus on the physical sciences for energy research is an approach that is complementary to the larger number of research groups and institutes that concentrate on engineering aspects of energy.

2016 was an excellent year for staff in SIRE. Congratulations are in order for two of our colleagues who were promoted to Personal Chairs in Chemistry: Professor Laurence Hardwick for his work on batteries and Professor Tony Lopez-Sanchez for his work on bio-feedstock and transformational chemistry.

Congratulations are also in order for Dr Jon Major who won an EPSRC Early Career Fellowship to pursue his work on improving the efficiency of low cost solar cells (read more about his work in the Research Projects section) and for research technician Vince Vasey, who has been promoted in recognition for his skill in keeping everyone’s research afloat in the labs.

As the Institute matures, it has been a bumper year for PhD graduations. Eight of our early stage research colleagues successfully defended their theses in 2016 and everyone in the team congratulates them and wishes them well in their future careers!

The Institute attracted two key energy conferences to Liverpool this year. The first was the UK flagship solar photovoltaics conference ‘PV Science and Technology’ with the local organisers being Dr Rob Treharne and colleagues. There were 110 papers, including an ever-increasing number from the field of ‘perovskite’ solar cells. You will find a conference report and an article about perovskites later in these pages.

The second was the international NanoEnergy Conference, with the local organisation being led by Dr Vin Dhanak. It attracted 125 delegates from 27 countries with the international flavour putting Brexit far from our minds! The opening address, given by former member of staff and Chancellor of the University (2007-2013) Professor Sir David King, is reproduced in full on page 4, and it set the tone for materials research taking the lead in shaping the future of world energy provision.

This year the Institute was proud to host a string of extended visits from research collaborators from India funded by the Research Councils UK Global Challenges Research Fund, including five visitors from the Indian Institute of Technology Delhi, National Institute of Technology (NIT) Durgapur and the Indian Institute of Science, Bangalore who wasted no time in making best use of our labs, and brought a lot of enthusiasm with them.

Our relationship with India is being cemented more widely. Dr Vin Dhanak was awarded an Indian Global Initiative of Academic Networks Fellowship and he made a return visit to NIT Durgapur to teach photoemission techniques to graduate students. The University’s special focus on India this year has left a good impression and an appetite for more collaborative work on energy topics.

Thank you for reading this annual report. I do hope that if you wish to know more or to collaborate with us, you will feel welcome to get in touch with any of the Institute’s experts using the directory of expertise at the back of this brochure.

Ken Durose.

Professor Ken Durose,
Director, SIRE

News, events and activities

Awards

Silvia Mariotti
For Best Poster, Photovoltaic Science and Technology 12, Liverpool, April 2016.

Congratulations to:

Dr Frédéric Blanc
For being promoted to Senior Lecturer in Chemistry.

Professor Laurence Hardwick
For the award of a Personal Chair in Chemistry.

Dr Vin Dhanak
For receiving a Government of India GIAN (Global Initiative of Academic Networks) teaching appointment.

Professor Tony Lopez-Sanchez
For the award of a Personal Chair in Chemistry.

Dr Gilberto Teobaldi
For becoming an Associated Member of the Beijing Computational Science Research Centre, Beijing, China and a visiting Professorship to the Solid State Physics Laboratory, Paris-Sud University, France.

Dr Jon Major
For winning an EPSRC (Engineering and Physical Sciences Research Council) Early Career Fellowship.

SIRE Seminar Series 2016

All staff in SIRE would like to extend their thanks to seminar speakers who have visited us in 2016.

Date	Name	Affiliation	Title
9.2.2016	**Professor Maria-Magdalena Titirici**	Department of Engineering and Materials Science, Queen Mary, University of London.	Sustainable Carbon Materials and Chemicals from Biomass Hydrothermal Processes
1.3.2016	**Professor Ken Durose**	Stephenson Institute for Renewable Energy and Department of Physics, University of Liverpool.	How to come top of the list with an EPSRC grant proposal
15.3.2016	**Dr Simon Beaumont**	Department of Chemistry, Durham University	In situ spectroscopy of catalytic materials
22.3.2016	**Dr Angela Cuesta**	Department of Chemistry, School of Natural and Computing Sciences, University of Aberdeen	Formic acid electrooxidation and The structure of ionic solvation shells An analysis based on in-situ ATR-SEIRAS.
3.5. 2016	**Professor Gleb Sukhorukov**	School of Engineering and Materials Science, Queen Mary University of London	Encapsulation and remote controlled delivery of active materials.
10.5.2016	**Professor Bettina Lotsch**	Max Planck Institute for Solid State Research, Germany	Towards rational catalyst design? Molecularly engineered frameworks for hydrogen evolution photocatalysis
29.11.2016	**Dr. Dr Paramaconi Rodriguez**	School of Chemistry, University of Birmingham	Expanding the boundaries of cathodic corrosion: The effective preparation of metal alloy nanoparticles and mixed oxides and their use as active electrocatalyst and photocatalyst

Our seminars are open to all comers and further details of the current programme may be found at: **www.liverpool.ac.uk/renewable-energy/events/**

Collaborations with India

Vin Dhanak

Global Challenge Research Funding

SIRE academics were awarded Global Challenge Research Funding (GCRF) through Overseas Development Aid to invite research fellows from India. The collaborating institutes in India included the Department of Physics, Indian Institute of Technology, Delhi, (IIT Delhi) and National Institute of Technology Durgapur, (NIT Durgapur). The funding allowed researchers to visit SIRE for a period of up to six months and was aimed at establishing and enhancing collaborations. The IIT Delhi fellow, Dr Saatviki Gupta, is engaged in preparation and characterisation of CZTS material for PV applications. Two students from NIT Durgapur have visited Dr Frank Jaeckel's group for a project on photocatalysis with nanomaterials.

Global Initiative of Academic Networks

The Government of India recently started a new program entitled Global Initiative of Academic Networks (GIAN) in Higher Education. The aim is to tap into the talent pool of scientists internationally, to encourage their engagement with the institutes of Higher Education in India so as to augment the country's existing academic resources, accelerate the pace of quality reform, and elevate India's scientific and technological capacity to global excellence. As part of this programme, Dr Vin Dhanak was awarded a GIAN fellowship to teach photoemission principle and application in PV materials characterization to post graduate students at the National Institute of Technology (NIT), Durgapur, West Bengal, India. The course attracted some 25 students from NIT as well as other institutes across West Bengal. This activity has strengthened our collaboration with NIT Durgapur.

Top: Sidarth Snadhya and Nilanjan Chakrabarty from NIT Durgapur working on photocatalysis in Dr Frank Jaeckel's group.

Bottom: Holly Edwards (SIRE PhD student) and Dr Saatviki Gupta from IIT Delhi, in the Nanomaterials Characterization Laboratory. Saatviki says "SIRE is an amazing place where young people like myself and Holly are given the freedom to explore their research ideas. Everyone here is welcoming and helpful, and every laboratory and facilities are accessible for our work. It is truly amazing and a great experience to be here."

NIT students in Durgapur, India at a problem class on photoemission, organised through the GIAN award to Dr Vin Dhanak.

EPSRC Early Career Fellowship awarded to Dr Jon Major on "Capacitance spectroscopy led process innovations to improve VOC in CdTe thin film solar cells".

Jon Major

Cadmium telluride (CdTe) solar cells offer an alternative to the current market leading silicon based photovoltaic (PV) modules. CdTe solar cells have lower materials costs and generate less CO_2 during production than Si. These modules are now in mass production and are already one of the lowest cost-per-watt solar technologies. Their continued development is however being limited by a failure to improve the generated voltage. This limit needs to be overcome in order reduce the cost per watt of power generation from solar and help end the need for a subsidised PV market. This fellowship seeks to identify a way to overcome this limitation.

The standard way to improve solar cell performance is through empirical process developments, optimising deposition conditions and techniques. This fellowship seeks to develop a different approach by using powerful capacitance spectroscopy techniques to identify routes to new process innovations. Capacitance spectroscopy allows electrically active defects, which are the cause of the voltage loss in CdTe solar cells, to be identified. By monitoring the number and position of these defects, linked to cell production and performance, we can identify both their source and their impact. This allows the key defects which most harm cell performance to be determined and thus process innovations to eliminate them can be developed. Through this physics-led approach to cell production we can overcome the voltage limitation in CdTe solar cells.

Whilst this project focuses on CdTe solar cells, the methodology established will have wider implications. There are a number of other solar cell technologies that have similar limitations and can benefit from the application of the techniques developed during this fellowship. The work undertaken in this project will benefit an entire generation of solar cells.

> *There are a number of other solar cell technologies that have similar limitations and can benefit from the application of the techniques developed during this fellowship.*

Activities of the EPSRC Centre for Doctoral Training in New and Sustainable Photovoltaics

Adam Mannis and Robert Treharne

The Centre for Doctoral Training in New and Sustainable Photovoltaics (CDT-PV) is in its third year of operation and now has a total of 37 PhD students engaged in specialised photovoltaics training and research across its seven academic partner institutions, led by Liverpool and Bath. A key success of the centre to date has been its high level of student interaction and student-led activities. Below we present a case study, submitted as part of a recent EPSRC mid-term review, that highlights the effectiveness of our cohort focused strategies to training.

EPSRC CENTRE FOR DOCTORAL TRAINING
NEW AND SUSTAINABLE
PHOTOVOLTAICS

EPSRC
Pioneering research and skills

Case Study: Ensuring Effective Cohort Building and Student Communication

The distributed, split-site operation of the CDT-PV (www.cdt-pv.org) could potentially have been a barrier to student training, but this has not been the case in reality. In fact, it is a key strength, since the CDT has used the programme of two-week institutional visits each month, from November to May for new starters, as a key mechanism to forge cohort interactions of much meaning and substance. They also interact beyond the cohort, with other CDTs and their peers in universities visited 'on tour'. These cohort relationships, personal and professional, then last for the duration of their studentships and beyond.

"During the seven months of [core-level] training, I travelled with my cohort between partner universities… I now have a much better idea of PV research going on at other universities and in companies around the UK… As for course content, I have received a detailed understanding of topics specialised to PV, gained lots of transferable skills, and made my own solar device … Living with the cohort for two week blocks over seven months was so much fun, and a great way of making friends from all over the country. We still keep in touch… The thing that really made the experience was the CDT-PV cohort, and I look forward to seeing everyone again each November along with a new intake of students." (Elizabeth Parrott, Cohort 1 student)

So, what makes this all work? A detailed handbook and kick-off Induction at the lead site (the University of Liverpool) sets the tone. This is linked to an annual CDT-PV Showcase event, with previous cohorts of students keen to be involved in the organisation and in also communicating their experiences during both the Induction and Showcase activities. These existing cohorts then pass on their advice and guidance to new arrivals. They, along with the CDT management team,

Cohort 1 students on a day trip to Isle of Wight during core-level training at the University of Southampton 2015.

make it very clear that the core-level training programme has a set of well-thought-out principles; explaining the rationale and setting expectations. New arrivals are informed that they can provide feedback on any element of their CDT experience, and that their opinions are valued for the development of a coherent programme relevant to the national PV community.

Cohort 3 students undertaking training in Python Coding with key CDT-PV partners Ossila Ltd, based at Sheffield University 2017.

The CDT-PV website facilitates student communication, both intra- and inter-cohort. It links together all the CDT's training content provided across the seven partner institutions. This is unique and substantial, as the archive of training content has been viewed thousands of times internationally; a public reach benefit. In addition, every CDT student has their own personal 'Portfolio' that they can use to update all of their specific project outputs (papers, posters, presentations), and can share these with others. An embedded electronic feedback system within the website also makes students feel part of the PV community.

It must be stated that consistency of training is a key principle that ensures cohort building takes place early at the CDT, especially as students move between the seven partner universities. This is achieved by having within each two-week component of core-level training a set of common principles that ensure: (i) lecture content is specific for PV and linked to robust assessments; (ii) hands-on activities are included encouraging joint working; (iii) time is devoted to an external industry-related group tour/visit; (iv) lab exercises promote the skilling of students in teams; (v) opportunities are available to give presentations to technical and non-technical audiences; and (vi) space is set aside at periods of each two-week block study for informal social gatherings.

What happens after the initial period of core-level training? "Slack" software is used by all cohorts to keep in touch around the country. It is a real-time discussion tool for teams, and we also use it to collect anonymous verbal feedback on training. It is used to follow-up on elements of feedback that have been received through our online portal, checking the scope for new opportunities and canvassing opinion of ongoing matters. The "Slack" tool also facilitates collaboration and dialogue on multiple topics such as researcher experiences, conferences, publications, etc. To date, there have been more than six thousand student interactions on topics by CDT-PV cohorts widely distributed on the "Slack" tool. In addition, all students meet up at research events, either those sponsored by the CDT or others related to PV. This further ensures associations and networks are strong across cohorts:

"From using my personal dedicated training budget, I have been able to present my research at events such as PVSAT and Clean Energy Live. The CDT was well represented by students from mine and other cohorts. We made sure to promote the CDT-PV brand while projecting a strong group identity of UK-funded research. This was also another means for us to meet as a PV cohort again." (Lewis Wright, Cohort 2 student)

SIRBATT Workshop ‘Controlling Lithium Battery Interfaces’, Orlando, USA

Laurence Hardwick

SIRE members involved: Laurence Hardwick (PI) (Glenda Wall – Project Manager, Gilberto Teobaldi, Ivan Scivetti, and Laura Cabo-Fernandez)

Delegates attending the SIRBATT Workshop in Orlando, Florida

SIRBATT (Stable Interfaces for Rechargeable Batteries) is led by Prof Laurence Hardwick within the Department of Chemistry at the Stephenson Institute for Renewable Energy.

The Project held its international Workshop *‘Controlling Lithium Battery Interfaces’* in Orlando, USA on 27th May 2016 which was attended by some 50 battery scientists.

Robert Kostecki from Lawrence Berkeley National Laboratory gave the keynote talk on *‘The mechanism of cathode dissolution in Li-ion batteries’*. Three guest speakers from the USA included Andrew Gewirth (University of Illinois); Christopher Johnson (Argonne National Laboratory) and Oleg Borodin (US Army Research Laboratories). Representatives from BACCARA, one of the other three successful projects with SIRBATT’s EC call, attended with talks from Lucile Quazaguel and Ekaterina Pavlenko outlining results from their project’s work.

Simon Malifarge from CNRS (France) who is currently working with the Renault car company gave a talk entitled *‘Influence of the design of high-energy-density graphite negative electrodes on the electrochemical performance’* and Eric De Vito working at CEA/University of Grenoble (France) spoke on his *‘Investigation of lithiation mechanisms and degradation of micrometric silicon composite electrodes’*. Seven SIRBATT partner institutions provided talks on their work within the project.

The University of Liverpool’s Department of Chemistry was well represented with the Hardwick Group’s Laura Cabo Fernandez speaking on *‘In situ Raman investigation of SEI (solid electrolyte interphase) growth on carbon-coated* $ZnFe_2O_4$ *anode material for Li-ion batteries’* and Christopher Sole giving a talk on *‘In situ observation of Li intercalation into graphitic flakes of varying layer number’*. Posters were presented by Iain Aldous, Thomas Galloway, Arturas Adomkevicius and Nicolas Drewett.

> *Talks and posters provided a wide overview of research currently being undertaken within the subject; and the Workshop ended with a summary and discussion of the current state of battery science across Europe and the USA.*

Talks and posters provided a wide overview of research currently being undertaken within the subject; and the Workshop ended with a summary and discussion of the current state of battery science across Europe and the USA. Future areas of research and possible exploitation were outlined and overall the event offered a unique opportunity for networking and collaboration within the wider international battery community.

SIRBATT – Final Report

Laurence Hardwick

SIRE members involved: Laurence Hardwick (PI), Glenda Wall (Project Manager) Gilberto Teobaldi, Ivan Scivetti and Laura Cabo-Fernandez

SIRBATT partners attending the European Commission's Final Meeting in Brussels

The SIRBATT Project (Stable Interfaces for Rechargeable Batteries) was a three-year £4 million European Commission (EC) funded network consisting of universities, research institutes and industry partners. The project was coordinated by Prof Laurence Hardwick from the Department of Chemistry and SIRE.

The EC held a final review of the work undertaken in Brussels on 3rd October 2016 during which time major contributors to the project, including Prof Hardwick and Dr Gilberto Teobaldi from SIRE, presented their work. The project aimed to achieve a radical improvement in the fundamental understanding of the structure and reactions occurring at the electrode/electrolyte interfaces of lithium-ion batteries, covering both experimental and theoretical aspects. This understanding is fundamental in developing strategies to boost the life-cycle and safety of lithium batteries. The European Commission (EC) considered that new insights had been reached through SIRBATT bringing the "next stage of battery development to innovative engineering, improved materials for the next generation of energy storage devices in addition to improving safety". They further considered that SIRBATT, had through the work led by Dr Gilberto Teobaldi, "demonstrated novel computational architectures capable of addressing the problems of the electrode/electrolyte interface for numerous investigation models for the anodes and cathodes utilised in contemporary battery technology".

The project also achieved innovative concepts concerning adoption of non-conventional lithium salts in the electrolyte formulation for next-generation electrolytes, obtained by the facile reaction route that showed stability toward various electrode materials. Their exploration, the EC considered, is already an "achievement beyond the state-of-the-art".

Studies on cycling stability in conventional, polymer and ionic liquid based electrolytes, which took place within the SIRBATT project, defined crucial factors governing the shelf life and cyclability of contemporary batteries. One of the main technical achievements of SIRBATT was the successfully built *in situ* setup for the investigation of Li metal-electrolyte interfaces, specifically dendrite growth, the ultimate safety concern of Li-metal anodes.

A unique goal of SIRBATT was to develop microsensors able to monitor simultaneously the temperature and pressure of lithium cells, maintaining optimum operating conditions thereby allowing longer lifetimes. Overall the EC considered that the project had "manufactured, tested and demonstrated the use of microsensors to a convincing level" and that the project had been "successfully accomplished".

SIRBATT's project management was highly praised by the EC who noted there was a strong lead from the coordinator. The large number of partners involved in the project made this task difficult, but the project management succeeded in showing a strong ability in managing the consortium, overseeing the scientific validation of results, directing the project development and in building strong relationships between partners.

The outputs from the project can be viewed at:
www.liverpool.ac.uk/sirbatt/publications

Photovoltaic Science and Technology Conference – PVSAT 2016

Attendees at PVSAT 12 in Liverpool

Liverpool did us proud! For some years now, PVSAT has claimed to be the UK's premier scientific conference on solar PV and I feel we have again justified this claim on the occasion of PVSAT-12, our 12th annual event. As initiated at last year's event in Leeds, we again held a Postdoctoral Training Workshop on the day preceding the conference so that student delegates could attend both events and keep costs down. This year for the first time PVSAT hosted a small workshop for the EU-funded project Steel PV to disseminate its work exploring the fabrication of PV cells on steel sheet for building integrated applications.

CDT PhD students Jack Swallow and Olivia Ashton check out the conference programme.

First the stats. This year 110 delegates listened to 8 presentations by invited international guest speakers, 32 contributory speakers and 37 poster presentations. Perovskite PV cells narrowly beat CdTe with 12 papers having the former in their title compared to 11 for the latter. Presentations on other PV semiconductor materials included CZTS (5 papers), CIGS (4), OPV (4), quantum dots (3), dye-sensitised (2), c-Si (2) and others (8).

Amongst many scientific highlights at the conference were a presentation by Prof Jan Schmidt (ISFH, Germany) on the potential of novel heterojunction solar cells including the possibility of 37% efficient tandem cells of perovskite on silicon. Intermediate band-gap solar cells with efficiency of 19.7% were reported by Peter Carrington (Lancaster) and single-walled carbon nanotube/PbS quantum dot cells with 6.5% efficiency reported by Yujiro Tazawa (Oxford).

Other keynote presentations included; PV integration into low-voltage distribution networks (Keith Sunderland, DIT Ireland), a new energy yield performance standard for PV modules (Markus Schweiger, TŰV, Germany), thin film PV for building integration (Yulia Galagan, TNO Host, The Netherlands) and life cycle assessment of PV (Mariska de Wild-Scholten, SmartGreenScans, The Netherlands). Two excellent presentations were given in the field of CdTe thin film cells by Prof Ken Durose (Liverpool) and Dr Wyatt Metzger (NREL, USA) who covered historic and current challenges with this technology.

Dan Lamb (Glyndŵr University) reported progress on a project to evaluate CdTe thin film cells in space satellites. Space cells are typically multi-junction devices based on III/V semiconductors but CdTe thin film PV offers exceptional high performance-to-weight ratio demanded for space application. The first flight test of these "made in Wales" cells is due for launch on 29 July 2016. We wish them a successful mission.

Whilst PVSAT has a predominantly science outlook, it is always helpful to view this in a commercial context and Dr Finlay Colville (Solar Media) gave an invited talk on market perspectives and insight into the challenge of the barrier-to-entry of new non-silicon PV cells in a market dominated by crystalline silicon technology.

The conference dinner was held in The Athenaeum, founded in 1797 to provide a meeting place where ideas and information could be exchanged. Today it is located in an elegant building erected in 1928 in the centre of Liverpool. Here we were entertained by live music performed by Liverpool Jazz and an amusing talk of his experiences with electric cars and the promotion of renewable energy by Robert Llewellyn (aka Kryten in Red Dwarf and host of Scrapheap Challenge).

Conference exhibitors included IET Journals, Newport, Kurt J Lesker and LOT Quantum Design.

PVSAT-12 is, as always, very grateful to our sponsors for supporting the event and helping to keep the student fee for conference attendance to a minimum. This year's sponsors included; IET Journals, Royal Society of Chemistry: Energy Sector Group, EPSRC SUPERGEN SuperSolar, SHARP, University of Liverpool, Steel PV and The Institute of Physics: Materials & Characterisation Group.

Nigel B Mason, Conference Chair
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NanoEnergy Conference 2016

Jon Major, Rob Treharne, Laurie Phillips and Ken Durose

The international NanoEnergy 2016 conference was held in the Central Teaching Hub at the University of Liverpool on 27-29 July 2016. The conference was organised by SIRE academics Dr Vin Dhanak, Dr Tim Veal, Professor Laurence Hardwick and Dr Ivona Mitrovic and attracted more than 125 delegates from 27 countries.

It was a great platform to highlight our work at the University and SIRE and covered a diverse field in energy conversion and storage. SIRE and the Physics department supported the conference, and 10 student bursaries were awarded from the SUPERGEN Supersolar Hub at Loughborough University to distribute to UK students. The conference opened with a keynote video address by Professor Sir David King. His speech is transcribed in full below:

Left: *NanoEnergy 2016 delegates in front of the Anglican Cathedral, the venue for the conference dinner.*
Top: *NanoEnergy 2016 delegates listening to the keynote address delivered by Prof Peter Edwards, University of Oxford.*
Bottom: *Prof Ken Durose (SIRE director) giving the after-dinner talk.*

"I would like to welcome the delegates to this important conference (NANOENERGY 2016). My own association with the University of Liverpool goes back some time, I am going to have to admit, it goes back to 1974 when I became a Chair of Physical Chemistry and subsequently I became the Chancellor of the University of Liverpool. As a professor of Physical Chemistry, I led a team working on surface science and of course Nanotechnology is the emerging science from surface sciences. I am delighted to say that the Stephenson Institute for Renewable Energy is a tremendous outcome from that work in those early days. The Stephenson Institute is focusing its work on what I call, and consider to be, the most important single topic for research across the world in this point in time. Of course I say that because my work in the Foreign Office today, but previously as a chief scientific advisor to the British government, has been heavily focused on the importance of climate change as a future threat to humanity. And managing that threat is a business of de-carbonising the global economy. Finding new technologies can aid that de-carbonising process through directive mission-oriented research and is a key way forward. I believe that the team assembled at Liverpool can play a very large part in that process. Energy storage activities, the key part of delivering new means of delivering renewable energy – and the overall process which needs to be integrated across all energy spheres. Creating energy from primary energy sources – solar, wind, geothermal – storing energy as needed because two of those sources are intermittent and then storing energy through smart grids and smart energy storage techniques. All of these processes together will replace the old fossil fuel industries. I think it is very important that we recognise the magnitude, not only of the challenge but of the opportunity this represents. The clean energy field is going to produce a market by 2020, an annual market of 3 to 6 trillion dollars a year. And addressing that is therefore an opportunity not only for dealing with this enormous challenge but also re-linking science, technology and wealth creation into delivering the solutions. So I think your work is not only critical but it has become a big part of what I have been working on since I joined the government in the foreign office nearly 3 years ago – and that is a programme called "Mission Innovation" and just a few words about "Mission Innovation" – it was the day of the 'COP' meeting (Paris Climate Conference) in Paris in early December last year (2015). Mission Innovation involves 22 nations plus the European Union committed to doubling their research funding of clean energy research by 2020. Not only is Britain a member of that grouping but a thought leader for that process. It was launched with President Obama, Modi, Prime Minister of India, President Hollande of France and our own British Prime Minister, together supporting those other nations. We've just had the first ministerial mission innovation in San Francisco at the beginning of this month and I am pleased to say that the total sum committed by the member nations will be 30 billion dollars per annum by 2020. This gives you an indication on how seriously the world's leaders are now taking the challenge of climate change. We need to work on this as a mission oriented programme and we need to be collaborative across laboratories, the Stephenson Institute, with other countries and other laboratories around the world to produce solutions to this enormous challenge. I believe we can do it, I believe time is short and we need to focus our efforts. I would like to wish you all a tremendous conference. This is such an important topic (Energy) and what you deliver is going to be a critical part of that process. Thank you."

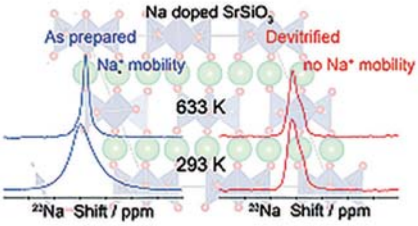
Selected research projects

Structure and Sodium Ion Dynamics in Sodium Strontium Silicate Investigated by Multinuclear Solid-State NMR

Frederic Blanc

Strontium silicate $SrSiO_3$ and alkali metal ('A-site' aliovalent substituents) solid solutions were recently investigated as potential intermediate temperature solid oxide fuel cell (SOFC) electrolytes. Initial reports proposed these materials as a new family of crystal structures able to permit rapid oxygen ion vacancy conductivity ($>10^{-1}$ S·cm^{-1} at 525°C), values which are in large excess of those previously reported in the classic fluorite and perovskite type oxides. However, this high oxide ion conductivity and the extremely unusual alkali metal substitution strategy have been extensively questioned in the literature. Here, we present a comprehensive understanding of the structure of one compound of this family, $Sr_{0.55}Na_{0.45}SiO_{2.775}$, using a combination of XRD and multinuclear ^{17}O, ^{23}Na, and ^{29}Si solid-state NMR spectroscopy data. A detailed investigation by high temperature NMR line shape analysis and relaxation rates measurements reveals that $Sr_{0.55}Na_{0.45}SiO_{2.775}$ is a sodium ion conductors and not an oxide ion conductors. Both ^{23}Na and ^{29}Si NMR spectra demonstrate the absence of Na doping in strontium silicate $SrSiO_3$ and the presence of an amorphous phase identified as $Na_2O{\cdot}2SiO_2$ glass as the Na-containing product. Devitrification at 800°C yields crystallization of the $Na_2O{\cdot}2SiO_2$ glass into the known crystalline α-$Na_2Si_2O_5$ phase which was positively identified by its XRD pattern and the extensive and clear ^{17}O, ^{23}Na, and ^{29}Si NMR fingerprints. High temperature ^{23}Na NMR reveals that the Na ions are mobile in the $Na_2O{\cdot}2SiO_2$ amorphous component below its glass transition temperature (~450°C). In contrast, ^{23}Na NMR data obtained on the crystalline α-$Na_2Si_2O_5$ shows limited Na dynamics below ~650°C (see figure below), and this result explains the large discrepancy in the conductivity observed in the literature which strongly depends on the thermal history of the $Sr_{0.55}Na_{0.45}SiO_{2.775}$ material. These insights demonstrate that the high conductivity observed in $Sr_{0.55}Na_{0.45}SiO_{2.775}$ is due to Na conduction in the $Na_2O{\cdot}2SiO_2$ glass, and this motivates the quest for the discovery of low temperature fast ion conductors in noncrystalline solids.

K.K. Inglis, J.P. Corley, P. Florian, J. Cabana, R.D. Bayliss, F. Blanc, *Structure and Sodium Ion Dynamics in Sodium Strontium Silicate Investigated by Multinuclear Solid-State NMR, Chem. Mater.* 28(11), 3850-3861 (2016).



Variable temperature ^{23}Na NMR spectra of as prepared $Sr_{0.55}Na_{0.45}SiO_{2.775}$ ($Na_2O{\bullet}2SiO_2$ and $SrSiO_3$) and devitrified $Sr_{0.55}Na_{0.45}SiO_{2.775}$ (α-$Na_2Si_2O_5$ and $SrSiO_3$). Reproduced with permission. Copyright 2016 American Chemical Society.

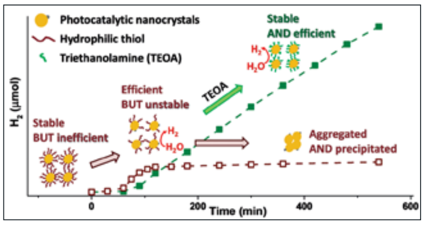
Optimising Stability and Efficiency in Colloidal Semiconductor Nanocrystals for Photocatalytic Hydrogen Generation

Frank Jaeckel

Colloidal semiconductor nanocrystals, decorated with co-catalyst clusters, are receiving great interest for their use in photocatalytic hydrogen generation using sunlight. This is mainly to their straightforward and low-cost fabrication as well as their tuneable optical and electronic properties. A major challenge, however, is to simultaneously achieve high stability and photocatalytic efficiency of the nanocrystals. Colloidal nanocrystals are typically protected by a shell of ligand molecules providing colloidal stability in solution. This very shell on the other hand frequently hinders interfacial charge transfer (here electron transfer to the co-catalyst and hole transfer to the hole scavenger) thereby reducing overall efficiency of hydrogen generation.

In this study, we replaced the original cysteine ligand shell in spherical, Pt-decorated CdS quantum dots in-situ with triethanolamine (TEOA) – a much more weakly bound ligand that maintains efficient interfacial charge transfer and thus photocatalytic efficiency and increases colloidal stability during photocatalytic hydrogen generation. The original cysteine ligands are replaced by TEAO which is being oxidised in the initial stages of the reaction as illustrated in the figure. The TEOA stabilised nanocrystals photocatalytically generate hydrogen more than ten times longer with similar efficiency to the original material (31.5% apparent quantum yield). Since TEOA is a cheap, commercially available ligand we expect this approach to be applicable to a range of colloidal nanomaterials for solar fuels generation.

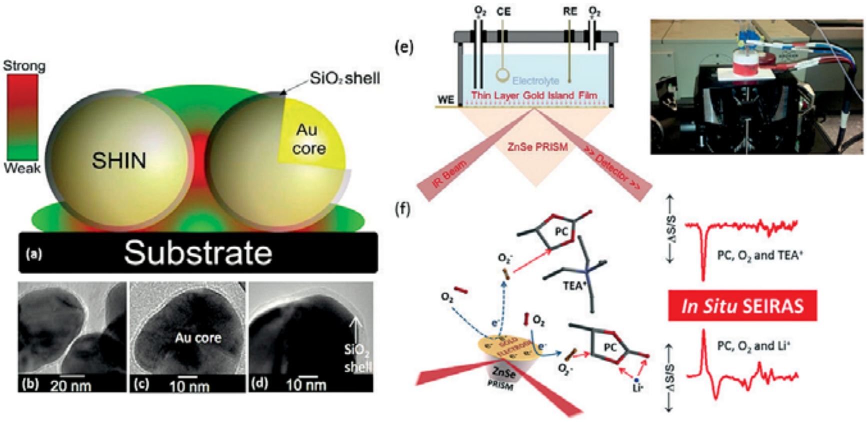
W. Li, J. Lee, F. Jäckel, *Simultaneous Optimization of Colloidal Stability and Interfacial Charge Transfer Efficiency in Photocatalytic Pt/CdS Nanocrystals* ACS Applied Materials & Interfaces, 8, 29434-29441 (2016).



The strategy for in-situ stabilisation of colloidal photocatalytic semiconductor nanocrystal systems. Reproduced with permission. Copyright The American Chemical Society 2016.

Advanced *In situ* Characterisation of Battery Materials

Laurence Hardwick



(a) A schematic diagram of the in situ electrochemical SHINERS method, illustrating the electromagnetic filed distribution between shell isolated nanoparticles (SHIN) on the electrode surface and (b-d) TEM images of SNINERS particle. (e,f) SEIRAS schematic and cell and example SEIRAS spectra for the propylene carbonate Li-O_2 systems, in which a ring opened species (RCO_2-) is detected.

Our group has developed a number of advanced *in situ* spectroelectrochemical techniques to probe the surface chemistries of metal-oxygen and lithium-ion batteries, and in 2016 we have published a series of papers that highlight our progress made in this area. Using surface enhanced Raman spectroscopy (SERS) we have established that in the sodium-air battery, high donor number solvents favour the formation of NaO_2 and low donor number solvents leading to surface Na_2O_2 films. Through shell isolated nanoparticles for enhanced Raman spectroscopy (SHINERS) we have demonstrated there is a substrate effect on the mechanism of the oxygen reduction reaction within non-aqueous electrolytes. We used surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) technique to show that the superoxide induced ring opening reaction of propylene carbonate is determined by the electrolyte cation. Understanding these mechanistic details are of significant importance toward a rational selection of the lithium-oxygen battery electrolytes.

Using *in situ* Raman spectroscopy, we have probed the electrode/electrolyte interface within a Li-ion cell by making use of the SERS effect induced by metal particles formed during $ZnFe_2O_4$ conversion reaction. Our discovery of this unusual *in situ* 'surface' and subsurface probe provides battery researchers with a sensitive tool to examine electrode film formation.

An *in situ* Raman spectro-electrochemical study of Li intercalation into graphite flakes with different thicknesses ranging from 1.7 nm (3 graphene layers) to 61 nm (ca. 178 layers) gave a Raman response indicative of increased tensile strain along the graphene sheet, as flake thickness decreased, during the early stages of intercalation. The implications for Li-ion batteries could be that intercalation induced strain from thinner flakes may accelerate carbon negative electrode ageing leading to a reduction of cycle life of the battery.

T.O. Galloway, L.J. Hardwick, *Utilizing in Situ Electrochemical SHINERS for Oxygen Reduction Reaction Studies in Aprotic Electrolytes*, J. Phys. Chem. Lett., 7, 2119 (2016)

I.M. Aldous, L.J. Hardwick, *Solvent-Mediated Control of the Electrochemical Discharge Products of Non-Aqueous Sodium-Oxygen Electrochemistry* Angew. Chem. Int. Ed., 55, 8254 (2016).

J. Padmanabhan Vivek, N.G. Berry, G. Papageorgiou, R.J. Nichols, L.J. Hardwick, *Mechanistic Insight into the Superoxide Induced Ring Opening in Propylene Carbonate Based Electrolytes using in situ Surface-Enhanced Infrared Spectroscopy*, J. Amer. Chem. Soc., 38 3745-3751 (2016)

L. Cabo-Fernandez, F. Mueller, S. Passerini, L.J. Hardwick, *In situ Raman spectroscopy of carbon-coated $ZnFe_2O_4$ anode material in Li-ion batteries – investigation of SEI growth* Chem. Commun., 52 3970 (2016)

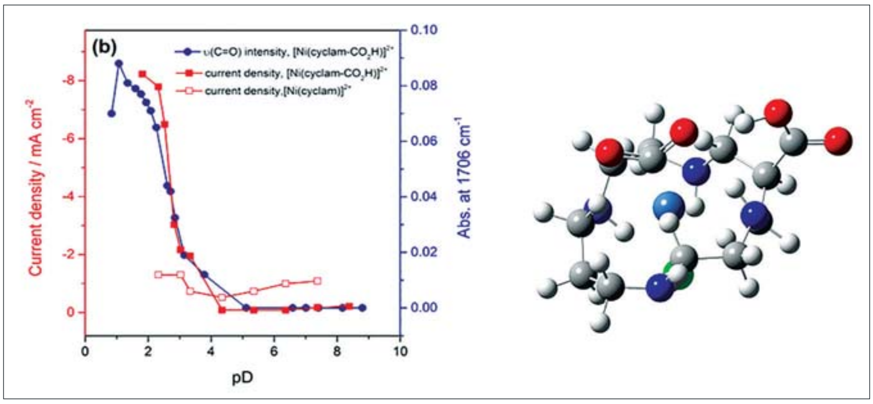
J. Zou., C. Sole., N.E. Drewett, M. Velický, L.J. Hardwick, *In Situ Study of Li Intercalation into Highly Crystalline Graphitic Flakes of Varying Thicknesses*, J. Phys. Chem. Lett., 7 4291 (2016).

Developing Active Electrocatalysts for the Reduction of Carbon Dioxide to Fuel Feedstocks in Water

Alex Cowan

Developing new catalysts for the reduction of carbon dioxide into fuels (e.g. methanol) or feedstocks (e.g. carbon monoxide) is an exciting opportunity to recycle a waste molecule back to a high value product. The electrochemical reduction of carbon dioxide also offers a potential route to addressing the intermittency of renewable energy resources. Excess electrical power from wind and solar generation can be used to drive the reduction of carbon dioxide to form a fuel which can be stored until needed.

To enable practical utilisation, carbon dioxide reduction electrocatalysts will need to be used in tandem with a sustainable oxidation reaction, such as water splitting. However this is challenging, the presence of water often leads to low selectivities towards carbon dioxide. Therefore it is important that new catalysts that operate in water under a range of conditions are developed. In this study we reported a development on a widely studied class of low cost nickel catalysts. The new catalyst synthesised shows remarkable levels of activity, reducing CO_2 over five times faster than the previous benchmark catalyst. Remarkably the new catalyst can even operate efficiently in acid solutions (pH 2) an important breakthrough that may have significant implications for enabling the development of CO_2 electrolysers..



Addition of pendant functionality on a nickel catalyst can lead to very high turnover frequencies for CO_2 reduction in acidic water.

G. Neri, I.M. Aldous, J.J. Walsh, L.J. Hardwick and A.J. Cowan. *"A highly active nickel electrocatalyst shows excellent selectivity for CO_2 reduction in acidic media."* Chemical Science 7(2): 1521-1526 (2016).

G. Neri, M. Forster, J.J. Walsh, C.M. Robertson, T.J. Whittles, P. Farràs and A.J. Cowan. *"Photochemical CO_2 reduction in water using a co-immobilised nickel catalyst and a visible light sensitiser."* Chemical Communications 52(99): 14200-14203 (2016).

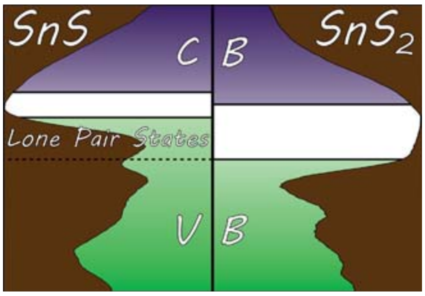
Band Alignments, Valence Bands, and Core Levels in the Tin Sulfides SnS, SnS_2, and Sn_2S_3: Experiment and Theory

Vin Dhanak and Tim Veal

Our group uses photoemission and inverse-photoemission to probe the density of filled and empty states in PV materials to investigate band-alignments and interfaces. As an example, this project studied, in collaboration with the groups of Dr Tim Veal and supported by theory from the group of Prof Aron Walsh (University of Bath), the different phases of tin sulphides were investigated. Generally tin sulfide solar cells show relatively poor efficiencies despite having properties attractive for photovoltaics, and there is difficulty in identifying separate phases, which are also known to form during Cu_2ZnSnS_2 (CZTS) depositions.

Here we present X-ray photoemission spectroscopy (XPS) and inverse photoemission spectroscopy measurements of single crystal SnS, SnS_2, and Sn_2S_3, with electronic-structure calculations from density functional theory (DFT). Differences in the XPS spectra of the three phases, including a 0.9 eV shift between the $3d_{5/2}$ peak for SnS and SnS_2, make this technique useful when identifying phase-pure or mixed-phase systems. Comparison of the valence band spectra from XPS and density functional theory reveals extra states at the top of the valence bands of SnS and Sn_2S_3 (see figure) arising from the hybridization of lone pair electrons in Sn(II), which are not present for the Sn(IV), as found in SnS_2. This results in relatively low ionization potentials for SnS (4.71 eV) and Sn_2S_3 (4.66 eV), giving a more comprehensive explanation as to the origin of the poor efficiencies. We also demonstrated, by means of a band alignment, the large band offsets of SnS and Sn_2S_3 from other photovoltaic materials and highlighted the detrimental effect on cell performance of secondary tin sulfide phase formation in SnS and CZTS films.

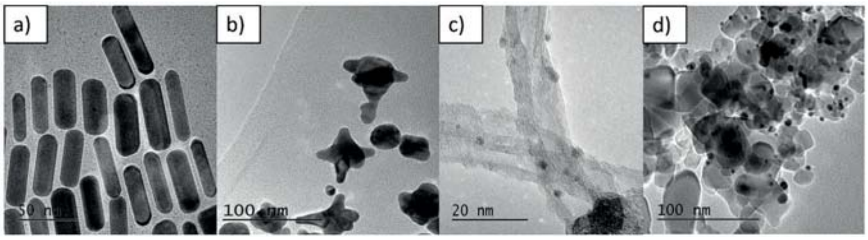
T.J. Whittles, L.A. Burton, J.M. Skelton, A.Walsh, T.D. Veal, V.R. Dhanak, *Band Alignments, Valence Bands, and Core Levels in the Tin Sulfides SnS, SnS_2, and Sn_2S_3: Experiment and Theory*, Chem. Mater., 28 (11), 3718-3726, (2016).



Valence band and conduction band edge of SnS and SnS_2, with the extra intensity in SnS attributed to lone pair electrons. The data from Sn_2S_3 (not shown here) are similar to SnS.

Alternative Routes for Biomass Valorisation using Catalysis, Microwaves and Light

Tony Lopez-Sanchez



Examples of catalysts utilised in the chemo and photoconversion of biomass derivatives: a) gold nanorods, b) gold nanostars, c) ruthenium in carbon nanotubes and d) gold-silver nanoaprticles on titania.

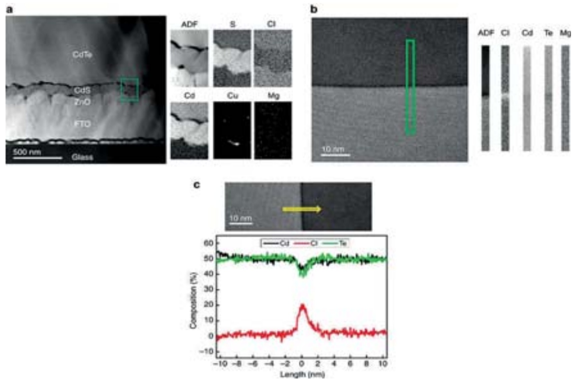
Valorising biomass offer many challenges that continuously tantalise scientists in the search of more efficient and creative ways to minimising the energy required and overall environmental footprint. We have seen the consolidation of biotechnology as a fundamental tool in biomass transformations, particularly due to the mild conditions typically required by enzymes and microorganisms. Thermochemical transformation technologies offer many advantages over bio-transformations, however, the high energetic requirements is still a draw-back. The utilisation of alternative energy vectors and *stimuli* to transform biomass, such as in the utilisation of microwave technology, sonochemistry or mechanochemistry offer some promise. However, could we possibly carry out demanding biomass transformations at very mild conditions without microorganisms or enzymes? The answer is yes, using light and catalysis. We have the vision that solar light will one day be used as the driving energy source to carry out the highly demanding upgrade of biomass under conditions similar to those used for bio-transformations, without the feed required by microorganisms. Our experiments recently demonstrated that it is possible to convert glucose to a range of partially oxidised products with 100% carbon mass balances with sunlight even on a cloudy day in Liverpool (UK) using cheap and unmodified TiO_2 as photocatalyst. We also found that plasmonic gold, silver and gold-silver alloyed nanoparticles promote the activity of titania in this reaction towards oxidation products. And more recently, we have demonstrated that selectivity can also be achieved when directly reacting cellobiose in one single process that breaks down the cellobiose glycosidic bond to yield glucose, but also formic acid in substantial yields using light at room temperature. On the other hand, our studies in combining microwaves with heterogeneous catalysis has resulted in the discovery of cheap, very active, stable and sustainable catalysts (Cu/TiO_2), that works at low temperatures (125°C) and low H_2 pressures for the furfural hydrogenation to furfuryl alcohol with unexpected enhancement in selectivity as compared to the reaction carried out at the same conditions using conventional heating. Furthermore, this work is a first example highlighting that using pressurized microwave reactors in the catalytic hydrogenation of biomass-derived compounds can offer huge advantages in terms of conversion and selectivity that could be determinant for commercial exploitation.

In Depth Analysis of Chloride Treatments for CdTe Solar Cells

Jon Major and Ken Durose

Cadmium telluride (CdTe) thin film solar cells have been reliant on what is commonly known as the chlorine activation step for over 30 years. This treatment is essential to achieve high performance solar cells. Despite being widely studied and being well established at the industrial level, the underlying origins of the benefit of the process are still not fully understood. This work took a different approach to understanding the process. Whereas in most published papers on the subject, a single chloride treatment (usually cadmium chloride), is normally studied, this work compared six different chloride processes. By comparing solar cells treated with chlorides that produced high solar cell efficiencies with those which did not we were able to resolve different aspects of the behaviour of the chloride treatment. We were able to conclusively prove that the primary role of the chloride treatment was to minimise the negative impact of grain boundaries, improving the materials properties and thereby increase the voltage generated by the solar cell. This work will help inform ways to improve the chlorine activation process. The study was done in collaboration with colleagues in Southampton, Durham, Vienna and umm al-Qura, Mecca.

J.D. Major, M.Al Turkestani, L.Bowen, M.Brossard, C.Li, P. Lagoudakis, S.J. Pennycook, L.J. Phillips, R.E. Treharne and K.Durose, *In-depth analysis of chloride treatments for thin-film CdTe solar cells* Nature Communications, 7, 13231 (2016).



STEM annular dark field (ADF) image of a cross section of a $MgCl_2$-treated CdTe solar cell, with EELS elemental maps from the region marked by a green box at (a) CdS/CdTe interface, (b) across a CdTe grain boundary and (c) electron energy loss spectroscopy (EELS) quantitative elemental profiles (from the position of the yellow arrow) for an $MgCl_2$-treated cell grain boundary. This data shows how chlorine preferentially accumulates at the grain boundaries changing the functionality of the solar cell.

Mild and Selective C-C Bond Activation in Arenes for Sustainable Synthesis of Fuel and Chemicals from Hydrocarbons

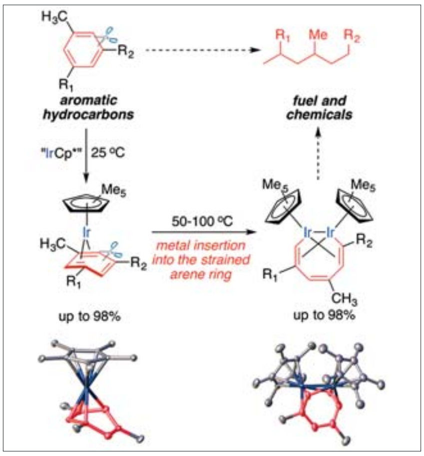
Alexey G. Sergeev

Many large-scale industrial processes for generation of fuel and chemicals from natural resources rely on catalytic cleavage of aromatic C-C bonds, the strongest bonds found in aromatic hydrocarbons. This transformation is typically conducted with metal catalysts that require harsh conditions (350-450°C) and lead to complex mixtures of products due to competing cleavage of other weaker C-H and C-C bonds. Design of milder and cleaner version of this process requires a conceptually new approach that enables facile and exclusive activation of aromatic C-C bonds by a metal centre.

We discovered such an approach that allows for mild and selective cleavage of aromatic C-C bonds by insertion of well-defined iridium complexes into the aromatic ring of alkyl arenes. The insertion occurs at 50-100°C without activation of weaker C-H and C-C bonds and gives unique metallacycles in high yields. The key for this unprecedented reactivity is the metal-induced bending of the arene ring, which creates a temporary ring strain and promotes direct and selective insertion of the metal into the otherwise inert arene ring C-C bonds.

Application of this approach for catalytic reductive cleavage of arenes has the potential to improve a range of industrial processes from direct coal liquefaction to valorisation of plant biomass. Finally, further elaboration of the induced ring strain concept would inspire design of novel arene functionalisations important for more efficient synthesis of pharmaceuticals and natural compounds.

M. Jakoobi, N. Halcovitch, G.F.S. Whitehead, and Alexey G. Sergeev, *Selective Arene Cleavage through Direct Insertion of Iridium into the Aromatic Ring* Angew. Chem. Int. Ed. 56 3266-3269 (2017).



Functionalisation of aromatic hydrocarbons through metal-mediated cleavage of arene ring C-C bonds.

Chemically Selective Alternatives to Photoferroelectrics for Polarization-Enhanced Photocatalysis: the Untapped Potential of Hybrid Inorganic Nanotubes

Gilberto Teobaldi

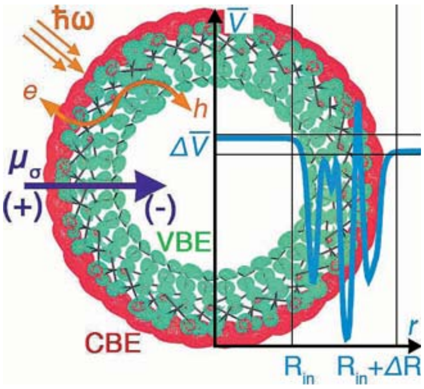
Photocatalytic materials (photocatalysts, PCs) can exploit solar light energy for chemical fuels production, pollutant degradation, or to access alternative, highly selective, reaction paths to high-value chemicals. The basic requirements of good (visible) light-absorbance, efficient separation of photogenerated electron-hole (e-h) pairs, independent e (h) diffusion to the PC-surfaces and transfer to (different or selected) reactants, are clearly established. However, fulfilment of such requirements by cheap and scalable materials remains elusive due to the poorly understood relationships between the properties of a PC and its atomic composition, structure, and solvent-dependent interactions with reactants.

Aiming at efficient e-h separation and diffusion to reactants, both one-dimensional (1D) structuring of PCs and use of permanently polarised photoferroelectrics have started to be explored and found to increase photocatalytic performance. Confinement of reactants inside nano-porous PCs has also been observed to benefit reaction selectivity. These, to date disconnected, advances raise the question as to whether the benefits of these different strategies could be integrated into one, ideally cheap, material.

Atomistic simulations of existing hybrid organic-inorganic nanotubes (NTs) suggest this to be the case. Based on the theoretical insights, generalizable strategies are proposed to increase the NT-polarisation for maximally enhanced electron-hole separation, while modulating independently the electrostatics inside the NT cavity, thence the electronic alignment with reactants and the e(h)-transfer kinetics.

Separate control of cavity electrostatics and polarisation-enhanced electron-hole separation may enable innovative strategies based on the use of local-polarisations in overall dipole-free (chemically selective) NTs to force reactants to match the photo-catalyst, as opposed to standard band-engineering of photo-catalysts for a given reactant.

D. Elliott, E. Poli, I. Scivetti, L.E. Ratcliff, L. Andrinopoulos, J. Dziedzic, N.D.M. Hine, A.A. Mostofi, C.K. Skylaris, P.D. Haynes and G. Teobaldi, *Chemically Selective Alternatives to Photoferroelectrics for Polarization-Enhanced Photocatalysis: The Untapped Potential of Hybrid Inorganic Nanotubes*. Adv. Sci. 3, 1600153 (2016).



Permanent dipole density (μ_σ) at the wall of open-ended, water-soluble inorganic imogolite nanotubes, and related interface potential step (ΔV), resulting in an electronegative cavity and an electropositive outer surface. These can be used to perturb interacting species (reactants, products and catalysts), their electronic levels and wavefunctions, therefore the overall energy drive and kinetics of the redox event.

Energy Nanocapsules for Heat Storage and Controlled Delivery

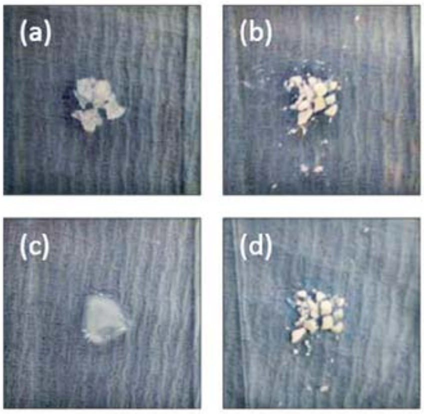
Dmitry Shchukin

Thermal energy storage has many important applications, and is most efficiently achieved by latent heat storage using phase change materials (PCMs). There are two types of the PCMs, which can be used for the heat storage and controlled release: organic long chain alkanes and inorganic salt hydrates. Both of them have their own pros and cons, and our group is working on the materials development to apply them in the areas most suitable for their chemical nature.

(i) Salt hydrates have advantages such as high energy storage density, high latent heat and incombustibility. However, they suffer from drawbacks such as incongruent melting and corrosion of container materials. By encapsulating them in a polymer shell, problems can be eliminated. We demonstrated a simple method to nanoencapsulate magnesium nitrate hexahydrate employing an *in situ* miniemulsion polymerisation with ethyl-2-cyanoacrylate as monomer. Using sonication to prepare mini-emulsions improved the synthesis by reducing the amount of surfactant required as stabiliser. The energy capsules are 100-200 nm in size, have salt hydrate located in the core and are stable over at least 100 thermal cycles with only a small (3%) reduction in latent heat. Supercooling is also drastically reduced. To the best of our knowledge, this is the first time an encapsulated salt hydrate PCM has been proven to have a lifetime of 100+ heat uptake/release cycles.

(ii) We introduced a new strategy to eliminate such convective heat transfer by inserting highly stable and conductive microcapsules into the electrothermal structures. The microcapsule is comprised of encapsulated long-chain alkanes and graphene oxide/carbon nanotube hybrids as shell material. Multiform carbon nanotubes in the microspheres stabilize the capsule shell to resist volume-change-induced rupture during repeated heating/cooling process; and meanwhile enhance the thermal conductance of encapsulated alkanes which facilitates an expeditious heat exchange. The resulting microcapsules can be homogeneously incorporated in the nanocarbon-based electrothermal structures. At a dopant of 5%, the working temperature can be enhanced by 30% even at a low voltage and moderate temperature, which indicates a great value in daily household applications.

M. Graham, E. Shchukina, P. Felix De Castro, D. Shchukin, *Nanocapsules containing salt hydrate phase change materials for thermal energy storage*, J. Materials Chemistry A 4, 16906-16912 (2016).



Mg(NO$_3$)$_2$.6H$_2$O (a & c) and nanoencapsulated salt hydrate (b & d) before heating to 100°C (**top**), and after letting them cool back to room temperature (**bottom**). Reproduced with permission. Copyright: Royal Society of Chemistry, J Mater. Chem A 4 (2016) 16906.

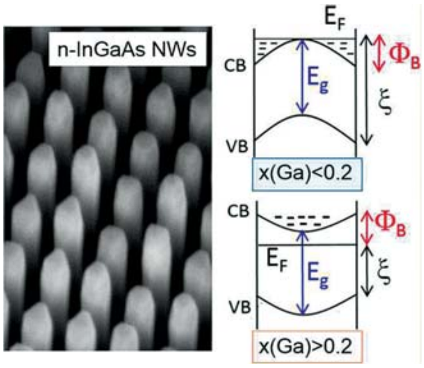
Z. Zheng, J. Jin, G.-K. Xu, J. Zou, U. Wais, A. Beckett, T. Heil, S. Higgins, L. Guan, Y. Wang, D. Shchukin, *Highly stable and conductive microcapsules for enhancement of joule heating performance*, ACS Nano 10, 4695–4703 (2016).

P. Felix De Castro, A. Ahmed, D. Shchukin, *Confined-volume effect on the thermal properties of encapsulated phase change materials for thermal energy storage*, Chemistry. A European Journal 22, 4389-4394 (2016).

Surface electronic properties and photoluminescence of semiconducting nanowires.

Tim Veal and Vin Dhanak

Semiconductor nanowires (NWs) are of tremendous interest for use in applications such as gas sensing, field effect transistors and solar cells. They feature a large surface area to volume ratio. Their surfaces are often invoked in explanations of optoelectronic properties, but the surface electronic properties are rarely studied directly. We investigated the composition dependence of Fermi level pinning at the surface and associated band bending effects in intrinsically n-type InGaAs NWs using correlated X-ray photoemission spectroscopy (XPS) and photoluminescence (PL). Comparison of the PL response of InGaAs NWs with and without the inherent native oxide reveals the existence two dominant radiative recombination pathways, direct near-band edge recombination and spatially indirect surface-state mediated recombination due to band bending and charge carrier accumulation/depletion at the NW surface. The energetic difference between the two radiative transitions changes significantly with composition, with the difference becoming smaller close to flat-band conditions. The band bending was further directly measured using XPS, revealing a clear transition from downward band bending/surface electron accumulation for high In-content InGaAs NWs (Fermi level pinned above the surface conduction band minimum) to upward band bending/surface electron depletion for higher Ga-content InGaAs NWs (Fermi level pinned in the band gap at the surface), with a crossover occurring close to 20% Ga, 80% In on the cation sub-lattice. These results provide very useful information for predicting the intrinsic conduction in InGaAs NWs, for selecting proper contacts to NWs and estimating the respective Schottky barrier heights, as well as for controlling internal quantum efficiencies in InGaAs NW-based optical devices.



Left: Scanning electron microscopy image of a representative InGaAs NW array (with 12% Ga, 88% In on the cation sub-lattice) depicted in tilted view (45°), illustrating the high uniformity of the NWs.
Right: The changes in surface band bending determined from XPS, from downward to upward bending toward higher Ga content. Published under a Creative Commons Attribution (CC-BY) License in Nano Letters 16, 5135 (2016)

M. Speckbacher, J. Treu, T. J. Whittles, W.M. Linhart, Xiaomo Xu, K. Saller, V.R. Dhanak, G. Abstreiter, J.J. Finley, T.D. Veal, and G. Koblmüller, *Direct Measurements of Fermi Level Pinning at the Surface of Intrinsically n-Type InGaAs Nanowires*, Nano Letters 16, 5135 (2016).

Surface X-ray Diffraction Studies of Single Crystal Electrocatalysts

Yvonne Grunder and Christopher Lucas

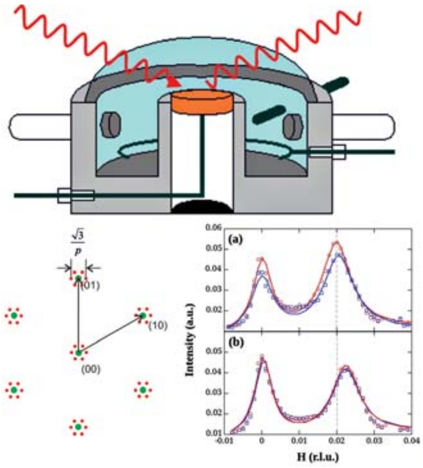
The ability of gold catalysts to promote the ability of adsorbed carbon monoxide to oxidise alcohols has been examined. It has been suggested that the presence of adsorbed CO can lead to OH adsorption at negative potentials in alkaline solution and this is the origin of the extraordinary electrocatalytic activity.

The Au(111) surface has been carefully analysed by surface X-ray diffraction (SXRD) in the potential range of the reconstruction in the absence and presence of CO. A systematic change in intensity, which can be correlated with a structural change, at exactly the same potential where the reversible peak in the CV was found after pre-adsorption of CO, is clearly observed. Given that it has been shown that the scattering from the surface reconstruction arises from a single atomic Au layer, the decrease in intensity can only be attributed to an increase in the disorder, i.e. buckling of the reconstructed Au layer.

The structural changes can be summarised as follows: In the absence of CO the surface is reconstructed with a value of p~25 at 0.25 V and undergoes in-plane compression as a function of the applied potential reaching p~24 at 0.7 V.

In the presence of CO no change in the surface compression is observed and the reconstruction is pinned into the (23 x √3) phase. Both with and without CO there is a decrease in the intensity of the reconstruction peak as the potential is increased. The intensity depends only on the density of the surface layer and the disordering (both thermal and static) which can be represented by a Debye-Waller factor. The decrease in intensity is associated with an increase in the surface buckling of the Au layer resulting in an increase in static disorder. The reconstruction peak intensity measured in the presence of CO is also lower than that observed in CO-free solution at any applied potential as this is the situation where the maximum compression (p~23) is observed.

The high resolution of the SXRD technique means that very subtle changes in the surface structure can be followed as a function of the applied electrode potential. It is observed that adsorbed CO blocks the in-plane lateral movement of the surface Au atoms (observed in the absence of CO), i.e. the reconstruction maintains a (23 x √3) structure, identical to the structure that is observed under UHV conditions, over the entire potential range.



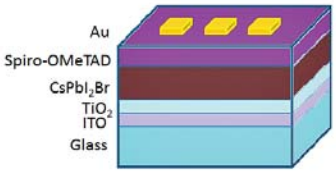
A sketch of the electrochemical cell employed for in-situ surface X-ray diffraction experiments is shown (top) together with a reciprocal space maps of the surface plane scattering observed for the Au(111) indicating where scattering from the reconstructed surfaces arises (bottom left). The bottom right panel shows the inplane X-ray diffraction from the reconstructed Au(111) surface measured along the [110] direction at 0.7 V and 0.25 V (vs RHE). (a) in 0.1 M KOH free of CO and (b) after CO adsorption at 0.25 V and purging of the electrolyte with N_2.

Perovskites – solar photovoltaic materials of the future?

Ken Durose

Recently the big news in solar electricity research has been about a new class of materials – inorganic/organic hybrids having the perovskite crystal lattice. Although they have been in the public eye for just a few years, they have achieved solar conversion efficiencies of nearly 20%. No other material in the history of solar cells comes close to this claim with traditional materials historically improving by only half a percent per year. So the ‘perovskites’ are indeed remarkable and are being touted as a possible replacement for the market leader, silicon. But it won’t be that simple: the leading perovskite material is unstable when exposed to UV light with oxygen and maybe water too. The material is methylammonium lead iodide, or $CH_3NH_3PbI_3$ – also known as MAPI. Other analogues of it have given similar results, but most of these also contain organic ions which are thought to participate in the unhelpful degradation. Silvia Mariotti, a Centre for Doctoral Training student in the Stephenson Institute, is trying a different approach. She is working on all-inorganic perovskite analogues in the hope that they will have higher stability. The material she has chosen is $CsPbI_2Br$, which like MAPI has the advantage that it can be solution processed, in this case from the caesium and lead iodides and bromides. Silvia has used this method to make full solar cell device structures (see figure) comprising glass/ITO/TiO_2/$CsPbI_2Br$/Spiro-OMeTAD/Au. So far these have given efficiencies of about 7%, open circuit voltages of 1.09 V and short circuit currents of 12.4 mA.cm^{-2}.

Moreover, the material is stable to the UV light and oxygen that degrade MAPI. However, Silvia’s exhaustive stability trials have found that $CsPbI_2Br$ is transformed into a non-photo active form by the presence of water. So if this compound were to be used for solar cells, they would need to be encapsulated. Remarkably though, the degradation of $CsPbI_2Br$ can be reversed simply by heating it. The recovered material can even be used to make excellent PV devices.



Solar cell structure using the $CsPbI_2Br$ perovskite material.

Silvia presented her work at the Photovoltaic Science and Technology conference (PVSAT) here in Liverpool in April, and was delighted to win the prize for ‘Best Poster’. She is continuing her work on $CsPbI_2Br$, as she believes that it can be optimised to make more efficient solar cell devices.

Publications by SIRE members in 2016

Catalysis and transformation

M.H. Ab Rahim, R.D. Armstrong, C. Hammond, N. Dimitratos, S.J. Freakley, M.M. Forde, D.J. Morgan, G. Lalev, R.L. Jenkins, J.A. Lopez-Sanchez. *"Low temperature selective oxidation of methane to methanol using titania supported gold palladium copper catalysts."* Catalysis Science & Technology 6(10): 3410-3418 (2016).

A.J. Cowan. *"Water oxidation Intermediate identification."* Nature Chemistry 8(8): 740-741 (2016).

L. Da Vià, C. Recchi, T.E. Davies, N. Greeves, J.A. Lopez-Sanchez. *"Visible-light-controlled oxidation of glucose using titania-supported silver photocatalysts."* ChemCatChem(22): DOI: 10.1002/cctc.201600775 (2016).

E.R. Draper, J.R. Lee, M. Wallace, F. Jäckel, A.J. Cowan, D.J. Adams. *"Self-sorted photoconductive xerogels."* Chemical Science 7(10): 6499-6505 (2016).

J.D. Elliott, E. Poli, I. Scivetti, L.E. Ratcliff, L. Andrinopoulos, J. Dziedzic, N.D.M. Hine, A.A. Mostofi, C-K. Skylaris, P.D. Haynes and G. Teobaldi. *"Chemically selective alternatives to photoferroelectrics for polarization-enhanced photocatalysis: The untapped potential of hybrid inorganic nanotubes."* Adv. Sci. 4 (2016).

W. Li, J.R. Lee and F. Jäckel. *"Simultaneous optimization of colloidal stability and interfacial charge transfer efficiency in photocatalytic Pt/CdS Nanocrystals."* ACS Applied Materials & Interfaces **8**(43): 29434-29441 (2016).

M. Lomeli-Rodriguez, M. Martín-Molina, M. Jiménez-Pardo, Z. Nasim-Afzal, S.I. Cauët, T.E. Davies and M. River-Toledo. *"Synthesis and kinetic modelling of biomass-derived renewable polyesters."* Journal of Polymer Science Part a-Polymer Chemistry **54**(18): 2876-2887 (2016).

A. Maneffa, P. Priecel and J.A. Lopez-Sanchez. *"Biomass-derived renewable aromatics: Selective routes and outlook for p-xylene commercialisation."* ChemSusChem **9**(19): 2736-2748 (2016).

T. Mavrič, M. Valant, M. Forster, A.J. Cowan, U. Lavrenčič and S. Emin. *"Design of a highly photocatalytically active ZnO/CuWO$_4$ nanocomposite."* Journal of Colloid and Interface Science **483**: 93-101 (2016).

G. Neri, I.M. Aldous, J.J. Walsh, L.J. Hardwick and A.J. Cowan. *"A highly active nickel electrocatalyst shows excellent selectivity for CO$_2$ reduction in acidic media."* Chemical Science **7**(2): 1521-1526 (2016).

G. Neri, M. Forster, J.J. Walsh, C.M. Robertson, T.J. Whittles, P. Farràs and A.J. Cowan. *"Photochemical CO$_2$ reduction in water using a co-immobilised nickel catalyst and a visible light sensitiser."* Chemical Communications **52**(99): 14200-14203 (2016).

E. Poli, J.D. Elliott, L.E. Ratcliff, L. Andrinopoulos, J. Dziedzic, N.D.M. Hine, A.A. Mostofi, C.K. Skylaris, P.D. Haynes and G. Theobaldi. *"The potential of imogolite nanotubes as (co-)photocatalysts: a linear-scaling density functional theory study."* Journal of Physics – Condensed Matter **28**(7): 1-17 (2016).

P. Priecel, H.A. Salami, R.H. Padilla, Z. Zhong and J.A. Lopez-Sanchez. *"Anisotropic gold nanoparticles: Preparation and applications in catalysis."* Chinese Journal of Catalysis **37**(10): 1619-1650 (2016).

P.N. Romano, J.M.A.R. de Almeida, Y. Carvalho, P. Priecel, E.F. Sousa-Aguiar and J.A. Lopez-Sanchez. *"Microwave-assisted selective hydrogenation of furfural to furfuryl alcohol employing a green and noble metal-free Cu Catalyst."* ChemSusChem **9**(24): 3387-3392 (2016).

R.S. Sprick, B. Bonillo, R. Clowes, P. Guiglion, N.J. Brownbill, B.J. Slater, F. Blanc, M.A. Zwijnenburg, D.J. Adams and A.I. Cooper. *"Visible-light-driven hydrogen evolution using planarized conjugated polymer photocatalysts."* Angewandte Chemie-International Edition **55**(5): 1824-1828 (2016).

T.V. Sviridova, L.Yu. Sadovskaya, E.M. Shchukina, A.S. Logvinovich, D.G. Shchukin and D.V. Sviridov. *"Nanoengineered thin-film TiO$_2$/h-MoO$_3$ photocatalysts capable to accumulate photoinduced charge."* Journal of Photochemistry and Photobiology a-Chemistry **327**: 44-50 (2016).

J.J. Walsh, C. Jiang, J. Tang and A.J. Cowan. *"Photochemical CO$_2$ reduction using structurally controlled g-C$_3$N$_4$."* Physical Chemistry Chemical Physics **18**(36): 24825-24829 (2016).

J.J. Walsh, J.R. Lee, E.R. Draper, S.M. King, F. Jäckel, M.A. Zwijnenburg, D.J. Adams and A.J. Cowan. *"Controlling visible light driven photoconductivity in self-assembled perylene bisimide structures."* Journal of Physical Chemistry C **120**(33): 18479-18486 (2016).

Y. Yang, M. Forster, Y. Ling, G. Wang, T. Zhai, Y. Tong, A.J. Cowan and Y. Li. *"Acid Treatment enables suppression of electron-hole recombination in hematite for photoelectrochemical water splitting."* Angewandte Chemie-International Edition **55**(10): 3403-3407 (2016).

Electrochemistry and electrochemical energy storage

I.M. Aldous and L.J. Hardwick. *"Solvent-mediated control of the electrochemical discharge products of non-aqueous sodium-oxygen electrochemistry."* Angewandte Chemie-International Edition 55(29): 8254-8257 (2016).

L. Cabo-Fernandez, F. Mueller, S. Passerini, L.J. Hardwick. *"In situ Raman spectroscopy of carbon-coated ZnFe$_2$O$_4$ anode material in Li-ion batteries – investigation of SEI growth."* Chemical Communications 52(20): 3970-3973 (2016).

S.Y. Chang, Y. Grunder, S.G. Booth, L.B. Molleta, A. Uehara, J.F.W. Mosselmans, G. Cibin, V.T. Pham, L. Nataf, R.A.W. Dryfe, S.L.M. Schroeder. *"Detection and characterisation of sub-critical nuclei during reactive Pd metal nucleation by X-ray absorption spectroscopy."* Cryst.Eng.Comm. 18(5): 674-682 (2016).

T.A. Galloway and L.J. Hardwick. *"Utilizing in situ electrochemical SHINERS for oxygen reduction reaction studies in aprotic electrolytes."* Journal of Physical Chemistry Letters 7(11): 2119-2124 (2016).

L.J. Hardwick. *"Batteries: avoiding oxygen."* Nature Energy **1**: 16115 (2016).

P. Harrison, C.I. Smith, Y. Grunder, C.A. Lucas, S.D. Barrett and P. Weightman. *"Anion replacement at Au(110)/electrolyte interfaces."* Physical Chemistry Chemical Physics 18(35): 24396-24400 (2016).

M. Liu, L. Chen, S. Lewis, S.Y. Chong, M.A. Little, T. Hasell, I.M. Aldous, C. M. Brown, M.W. Smith, C.A. Morrison, L.J. Hardwick and A.I. Cooper. *"Three-dimensional protonic conductivity in porous organic cage solids."* Nature Communications **7** (2016).

C.A. Lucas, F. Maroun, N. Sisson, P. Thompson, Y. Gründer, R. Cortès and P. Allongue. *"Film and interface atomic structures of electrodeposited Co/Au(111) layers: An in situ X-ray scattering study as a function of the surface chemistry and the electrochemical potential."* Journal of Physical Chemistry C **120**(6): 3360-3370 (2016).

Publications

(Continued)

B.J. Morgan, J. Carrasco and G. Teobaldi. *“Variation in surface energy and reduction drive of a metal oxide lithium-ion anode with stoichiometry: a DFT study of lithium titanate spinel surfaces.”* Journal of Materials Chemistry A **4**: 17180-17192 (2016).

N. Sisson, Y. Gründer and C.A. Lucas. *“Structure and stability of underpotentially deposited Ag on Au(111) in Alkaline Electrolyte.”* Journal of Physical Chemistry C **120**(29): 16100-16109 (2016).

C.I. Smith, P. Harrison, C.A. Lucas, Y. Grunder, S.D. Barrett and P. Weightman. *“The stability of the Au(110)-(1 x 3) surface reconstruction in electrochemical environments.”* Journal of Physics-Condensed Matter **28**(1): 1-7 (2016).

J.P. Vivek, N. Berry, G. Papageogiou, R.J. Nichols and L.J. Hardwick. *“Mechanistic insight into the superoxide induced ring opening in propylene carbonate based electrolytes using in situ surface-enhanced infrared spectroscopy.”* Journal of the American Chemical Society **138**(11): 3745-3751 (2016).

J. Zou, C. Sole, N.E. Drewett, M. Velický and L.J. Hardwick. *“In situ Li intercalation into highly crystalline graphitic flakes of varying thicknesses.”* Journal of Physical Chemistry Letters **7**(21): 4291-4296 (2016).

Electronic and magnetic materials

A. Ahmed, C.M. Robertson, A. Steiner, T. Whittles, A. Ho, V. Dhanak and H. Zhang. *“Cu(I)Cu(II)BTC, a microporous mixed-valence MOF via reduction of HKUST-1.”* RSC Advances 6(11): 8902-8905 (2016).

S. Chakraborty, S. Saha, V.R. Dhanak, K. Biswas, M. Barbezat, G.P. Terrasi, A.K. Chakraborty. *“High yield synthesis of amine functionalized graphene oxide and its surface properties.”* RSC Advances 6(72): 67916-67924 (2016).

D. Curcio, E. Miniussi, P. Lacovig, S. Lizzit, R. Larciprete, J.A. Smerdon, V.R. Dhanak, R. McGrath, A. Baraldi. *“Crystal to quasicrystal surface phase transition: An unlocking mechanism for templated growth.”* Journal of Physical Chemistry C 120(10): 5477-5485 (2016).

W.M. Linhart, M.K. Rajpalke, J. Buckeridge, P.A.E. Murgatroyd, J.J. Bomphrey, J. Alaria, C.R.A. Catlow, D.O. Scanlon, M.J. Ashwin and T.D. Veal. *“Band gap reduction in InN_xSb_{1-x} alloys: Optical absorption, k.P modeling, and density functional theory.”* Applied Physics Letters **109**(13): 132104-1 - 132104-5 (2016).

P. Mandal, M.J. Pitcher, J. Alaria, H. Niu, M. Zanella, J.B. Claridge and M.J. Rosseinsky. *“Controlling phase assemblage in a complex multi-cation system: phase-pure room temperature multiferroic $(1-x)BiTi(_{1-y})/_{2}Fe_{y}Mg(_{1-y})/_{2}O_{3-x}CaTiO_{3}$.”* Advanced Functional Materials **26**(15): 2523-2531 (2016).

M. O’Sullivan, J. Hadermann, M.S. Dyer, S. Turner, J. Alaria, T.D. Manning, A.M. Abakumov, J.B. Claridge and M.J. Rosseinsky. *“Interface control by chemical and dimensional matching in an oxide heterostructure.”* Nature Chemistry **8**(4): 347-353 (2016).

A. Shaw, J.S. Wrench, J.D. Jin, T.J. Whittles, I.Z. Mitrovic, M. Raja, V.R. Dhanak, P.R. Chalker and S. Hall . *“Atomic layer deposition of Nb-doped ZnO for thin film transistors.”* Applied Physics Letters **109**(22): 222103-1 - 222103-4 (2016).

M. Speckbacher, J. Treu, T.J. Whittles, W.M. Linhart, X. Xu, K. Saller, V.R. Dhanak, G. Abstreiter, J.J. Finley, T.D. Veal and G. Koblmüller. *“Direct measurements of fermi level pinning at the surface of intrinsically n-type InGaAs nanowires.”* Nano Letters **16**(8): 5135-5142 (2016).

Heat storage materials and microcapsules

D. Grigoriev, E. Shchukina, A. Tleuova, S. Aidarova, D.G. Shchukin. *“Core/shell emulsion micro- and nanocontainers for self-protecting water based coatings.”* Surface and Coatings Technology 303 299–309 (2016).

D.G. Shchukin and E. Shchukina. *“Application of clay materials as nanocontainers for self-healing coatings.”* Royal Society of Chemistry www.rsc.org: 223-244 (2016).

P.F. De Castro, A. Ahmed, D.G. Shchukin. *“Confined-volume effect on the thermal properties of encapsulated phase change materials for thermal energy storage.”* Chemistry-A European Journal 22(13): 4389-4394 (2016).

M. Graham, E. Shchukina, P. Felix De Castro, D.G. Shchukin. *“Nanocapsules containing salt hydrate phase change materials for thermal energy storage, J. Mater.”* Chem. A4 4: 6 (2016).

G.L. Li, R. Yu, T. Qi, H. Möhwald, and D.G. Shchukin. *“Double-shelled polymer nanocontainers decorated with poly(ethylene glycol) brushes by combined distillation precipitation polymerization and thiol-yne surface chemistry.”* Macromolecules 49(3): 1127-1134 (2016).

T.V. Sviridova, L.Y. Sadovskaya, E. Shchukina, A.S. Logvinovich, D.G. Shchukin, D.V. Sviridov: *Nanoengineered Thin-Film TiO_2/h-MoO_3 Photocatalysts Capable to Accumulate Photoinduced Charge, J. of Photochem. & Photobiology A: Chemistry,* **327**, 44-50 (2016).

Y. Wang, Y. Zhu, C. Li, D. Song, T. Zhang, X. Zheng, Y. Yan, M. Zhang, J. Wang and D.G. Shchukin. *“Smart epoxy coating containing Ce-MCM-22 zeolites for corrosion protection of Mg-Li alloy.”* Applied Surface Science **369**: 384-389 (2016).

Z. Zheng, J. Jin, G-K. Xu, J. Zou, U. Wais, A. Beckett, T. Heil, S. Higgins, L. Guan, Y. Wang and D. Shchukin. *“Highly stable and conductive microcapsules for enhancement of joule heating performance.”* ACS Nano **10**(4): 4695-4703 (2016).

Solar energy materials and solar cells

H Bayhan, S. Özden, J.D. Major, M. Bayhan, E.T. Dagdeviren, K. Durose. *“A comparison of the effect of $CdCl_2$ and $MgCl_2$ processing on the transport properties of n-CdS/p-CdTe solar cells and a simple approach to determine their back contact barrier height.”* Solar Energy 140 66–72 (2016).

L.A. Burton, T.J. Whittles, D. Hesp, W.M. Linhart, J.M. Skelton, B. Hou, R.F. Webster, G. O’Dowd, C. Reece, D.J. Fermin, T.D. Veal, V.R. Dhanak, A. Walsh. *“Electronic and optical properties of single crystal SnS2: an earth-abundant disulfide photocatalyst.”* Journal of Materials Chemistry A 4(4): 1312-1318 (2016).

Y.G. Fedorenko, J.D. Major, A. Pressman, L. Phillips, K. Durose. *“Electronic properties of CdS/CdTe solar cells as influenced by the choice of a buffer layer.”* MRS Advances: (2016).

S. Gupta, T.J. Whittles, Y. Batra, V. Satsangi, S. Krishnamurthy, V.R. Dhanak, B.R. Mehta. *“A low-cost, sulfurization free approach to control optical and electronic properties of Cu_2ZnSnS_4 via precursor variation.”* Solar Energy Materials and Solar Cells 157: 820-830 (2016).

J. Jin, J. Zhang, R.E. Kemal, Y. Luo, P. Bao, M. Althobaiti, D. Hesp, V.R. Dhanak, Z. Zheng, I.Z. Mitrovic, S. Hall, A. Song. *“Effects of annealing conditions on resistive switching characteristics of SnO_x thin films.”* Journal of Alloys and Compounds 673: 54-59 (2016).

G. Kartopu, L.J. Phillips, V. Barrioz, S.J.C. Irvine, S.D. Hodgson, E. Tejedor, D. Dupin, A.J. Clayton, S.L. Rugen-Hankey and K. Durose. *"Progression of metalorganic chemical vapour-deposited CdTe thin-film PV devices towards modules."* Progress in Photovoltaics 24(3): 283-291 (2016).

J. Major. *"Grain boundaries in CdTe thin film solar cells: a review."* Semiconductor Science and Technology **31**: 19pp (2016).

J.D. Major, M. Al Turkestani, L. Bowen, M. Brossard, C. Li, P. Lagoudakis, S.J. Pennycook, L.J. Phillips, R.E. Treharne, K. Durose. *"In-depth analysis of chloride treatments for thin-film CdTe solar cells."* Nature Communications 7 (2016).

B.G. Mendis, A. Howkins, D. Stowe, J.D. Major, K. Durose. *"The role of transition radiation in cathodoluminescence imaging and spectroscopy of thin-foils."* Ultramicroscopy **167**: 31-42 (2016).

B.G. Mendis, R.E. Treharne, D.W. Lane and K. Durose. *"The effects of junction interdiffusion and misfit dislocations on the efficiency of highly mismatched heterojunction photovoltaic devices."* Applied Physics Letters **108**(18): 183505-1 - 183505-5 (2016).

G. Papageorgiou, J.D Major, K. Durose. *"Substrate geometry CdTe solar cells with catalytically-grown nano-rough surfaces."* 5 (2016).

L.J. Phillips, A.M. Rashed, R.E. Treharne, J. Kay, P. Yates, I.Z. Mitrovic, A. Weerakkody, S. Hall and K. Durose. *"Maximizing the optical performance of planar* $CH_3NH_3PbI_3$ *hybrid perovskite heterojunction stacks."* Solar Energy Materials and Solar Cells **147**: 327-333 (2016).

M.J. Wahila, K.T. Butler, Z.W. Lebens-Higgins, C.H. Hendon, A.S. Nandur, R.E. Treharne, N.F. Quackenbush, S. Sallis, K. Mason, H. Paik, D.G. Schlom, J.C. Woicik, J. Guo, D.A. Arena, B.E. White Jr., G.W. Watson, A. Walsh and L.F.J. Piper. *"Lone-pair stabilization in transparent amorphous tin oxides: A potential route to p-type conduction pathways."* Chemistry of Materials **28**(13): 4706-4713 (2016).

T.J. Whittles, L.A. Burton, J.M. Skelton, A. Walsh, T.D. Veal and V.R. Dhanak. *"Band alignments, valence bands, and core levels in the tin sulfides SnS,* SnS_2*, and* Sn_2S_3*: Experiment and theory."* Chemistry of Materials **28**(11): 3718-3726 (2016).

Solid state NMR and spectroscopy

E.F. Baxter, T.D. Bennett, A.B. Cairns, N.J. Brownbill, A.L. Goodwin, D.A. Keen, P.A. Chater, F. Blanc and A.K. Cheetham. *"A comparison of the amorphization of zeolitic imidazolate frameworks (ZIFs) and aluminosilicate zeolites by ball-milling."* Dalton Transactions 45(10): 4258-4268 (2016).

T.D. Bennett, Y.Z. Yue, P. Li, A. Qiao, H.Z. Tao, N.G. Greaves, T. Richards, G.I. Lampronti, S.A.T. Redfern, F. Blanc, O.K. Farha, J.T. Hupp, A.K. Cheetharm, D.A. Keen. *"Melt-quenched glasses of metal-organic frameworks."* Journal of the American Chemical Society 138(10): 3484-3492 (2016).

D.M. Halat, R. Dervişoğlu, K. Gunwoo, M.T. Dunstan, F. Blanc, D.S. Middlemiss and C.P. Grey. *"Probing oxide-ion mobility in the mixed ionic-electronic conductor* $La_2NiO_{4+\delta}$ *by Solid-State O-17 MAS NMR Spectroscopy."* Journal of the American Chemical Society 138(36): 11958-11969 (2016).

K.K. Inglis, J.P. Corley, P. Florian, J. Cabana, R.D. Bayliss and F. Blanc. *"Structure and sodium ion dynamics in sodium strontium silicate investigated by multinuclear Solid-State NMR."* Chemistry of Materials 28(11): 3850-3861 (2016).

F.G. Kinyanjui, S.T. Norberg, C.S. Knee, I. Ahmed, S. Hull, L. Buannic, I.Hung, Z. Gan, F. Blanc, C.P. Grey and S.G. Eriksson. *"Crystal structure and proton conductivity of* $BaSn_{0.6}Sc_{0.4}O_{3-\delta}$*: insights from neutron powder diffraction and solid-state NMR spectroscopy."* Journal of Materials Chemistry A 4(14): 5088-5101 (2016).

A.B. Santibáñez-Mendieta, C. Didier, K.K. Inglis, A.J. Corkett, M.J. Pitcher, M. Zanella, J. Felix Shin, L.M. Daniels, A. Rakhmatullin, M. Li, M.S. Dyer, J.B. Claridge, F. Blanc and M.J. Rosseinsky. *"*$La_3Li_3W_2O_{12}$*: Ionic Diffusion in a Perovskite with Lithium on both A- and B-Sites."* Chemistry of Materials **28**(21): 7833-7851 (2016).

Theory (further theory papers are presented in the sections above)

G. Moynihan, G. Teobaldi and D.D. O'Regan. *"Inapplicability of exact constraints and a minimal two-parameter generalization to the DFT+U based correction of self-interaction error."* Physical Review B **94**: 220104-1 - 220104-6 (2016).

D.D. O'Regan and G. Teobaldi. *"Optimization of constrained density functional theory."* Physical Review B **94**(3): 035159-1 - 035159-14 (2016).

D.H.P. Turban, G. Teobaldi, D.D. O'Regan and N.D.M. Hine. *"Supercell convergence of charge-transfer energies in pentacene molecular crystals from constrained DFT."* Physical Review B **93**(16): 165102-1 - 165102-8 (2016).

Patents

Selective oxygenation of alkanes using oxygen

G.J. Hutchings, M.M. Forde, J.A. Lopez-Sanchez, N. Dimitratos, N. Dimitratos

US Patent 9,428,454

PhD Theses

Iain Aldous, Non-aqueous Spectroelectrochemistry of Dioxygen for Alkali Metal-Oxygen Batteries (Prof L Hardwick)

Mohammed Althobiti, Characterizing High-k Materials on Germanium (Dr V Dhanak)

Max Birkett, Optical properties of Earth-abundant Semiconductors for Renewable Energy (Dr T Veal)

Luigi DaVia, Photocatalytic Oxidation of Glucose and Cellobiose using Titanium Oxide Supported Bimetallic Nanoparticles (Prof J Lopez-Sanchez)

Joshua D. Elliott, The Application of Linear-scaling Density Functional Theory to Large Metal Oxide Nanotubes (Dr G Theobaldi)

Joel McGlone, Microwave Synthesis of H-ZSM-5, H-Beta and H-Y and their Desilication and Templation to Hierarchical Structures for Friedel-Crafts Alkylation and Diels-Alder Cycloaddition (Prof J Lopez-Sanchez)

Enzo Peccerillo, $CuSbS_2$ and Related Chalcogenides for Sustainable Photovoltaics (Prof K Durose)

Tzu-Ho Wu, Optimising Cell Voltage and Understanding Charge Storage Mechanism of Transition Metal Oxides and Hydroxides for Aqueous Supercapacitors (Prof L Hardwick)

Research funding
held in 2016

SIRE hold more than £15,000,000 in active grants. New grants added in 2016 are marked with an asterisk:

Engineering and Physical Sciences Research Council	Funding
J. Alaria, X-ray diffraction capability for nanoscale and thin film structure**	£360,018
J. Alaria, Layered oxide thermoelectrics for high temperature waste heat recovery*	£100,579
F.. Blanc, EPSRC Institutional Sponsorship 2016*	£11,737
F.. Blanc, Dynamic nuclear polarization solid-state nuclear magnetic resonance spectroscopy of intensive nuclear spins	£60,624
A.J. Cowan, CO_2 reduction at high pressures*	£8,000
A.J. Cowan, Spectroscopy-driven design of an efficient photocatalyst for carbon dioxide reduction	£885,066
K. Durose, EPSRC Centre for Doctoral Training in New and Sustainable Photovoltaics	£5,260,808
K. Durose, SUPERSOLAR Solar Energy Hub	£ 337,851
K. Durose, SUPERSOLAR flexible funding-planar heterojunctions for perovskite-based PV: optical design, heterostructure screening and junction properties*	£120,237
K. Durose, University of Liverpool – equipment account (CDT)	£42,000
K. Durose, Overcoming the grain size limit to Voc in sustainable photovoltaics	£508,351
K. Durose, V. Dhanak, EPSRC Global Challenges Research Fund Award 2016 (UoL)*	£14,000
K. Durose, L. Hardwick, EPSRC Global Challenges Research Fund Award 2016 (UoL)*	£10,000
K. Durose, F. Jaeckel, R. Potter EPSRC Global Challenges Research Fund Award 2016 (UoL)*	£14,000
L.J. Hardwick, Impact Acceleration Account – University of Liverpool 2012	£20,000
L.J. Hardwick, Growth and dissolution mechanism of metal oxides in metal-air batteries*	£95,557
L.J. Hardwick, Multi-scale analysis for facilities for energy storage (manifest)*	£89,274
L.J. Hardwick, The role of electrocatalysts in the oxygen reduction reaction in non-aqueous electrolytes	£354,296
L.J Hardwick, Electrochemical energy storage with graphene-enables materials	£642,250
J.A Lopez-Sanchez, Impact Acceleration Account – University of Liverpool 2012	£19,570
J.A. Lopez-Sanchez, Renewable chemicals from sustainable feedstocks via high-throughput methods	£1,042,294
J.A. Lopez-Sanchez, Bio-renewable formulation information and knowledge management system	£20,167
J.D. Major, Capacitance spectroscopy led process innovations to improve VOC in CdTe thin film solar cells*	£810,101
J.D. Major, Advanced electrical characterisation of thin film PV structures	£6,688
R. Nichols, S. Higgins, F. Jaeckel, Single-Molecule Plasmoelectronics	£444,776
T.D. Veal, Donor design for maximum mobility transparent conducting oxides	£377,292

Innovate (UK)	Funding
L.J. Hardwick, Practical lithium air batteries*	£95,087
D. Shchukin, Innovative assembly processes and equipment for healthier foods emulsions and new market opportunities*	£264,004

Royal Society	Funding
F. Blanc, Spectroscopic structural investigation of La doped SrTi03 anodes*	£11,944
Y. Grunder, Alternative solvents for electrochemical processes*	£1,000
Y. Grunder, Electrochemistry in non-aqueous solvents	£134,337
Y. Grunder, Alternative solvents for electrochemical processes	£1,450
L.J. Hardwick, Electrochemistry and *in situ* spectroscopy of asymmetric supercapacitors	£12,000
A. Sergeev, Iridium-catalyzed selective reductive cleavage of unstrained C-C bonds: insight into the catalytic cycle*	£2,368
A. Sergeev, Selective reduction of arenes to alkanes by assisted tandem catalysis	£14,807
G. Teobaldi, Advanced new linear-scaling constrained density-functional theory approaches	£11,995

European Commission	Funding
K. Durose, NanoBarrier – Embracing one dimensional semiconductor nanostructures	£233,886
L.J. Hardwick, SIRBATT – Stable interfaces for rechargeable batteries	£695,501
D. Shchukin, NonaBarrier – Extended shelf-life biopolymers for sustainable and multifunctional food packaging solutions	£420,952
D. Shchukin, BYEFOULING – Low-toxic cost-efficient environment-friendly antifouling materials	£161,286
D. Shchukin, SONO ENGINEERING – Electronic structures sono-engineering of semiconductor nanoparticle for efficient solar energy exploitation	£185,340
*D. Shchukin, ENERCAPSULE – Nanoencapsulation for energy storage and controlled release	£1,594,670

Science and Technology Facilities Council	Funding
F. Blanc, Probing lithium conduction pathways in fast lithium ion electrolytes for all solid-state Li batteries by high temperature 7Li pulsed-field gradient NMR spectroscopy	£3,000

Other Sponsors	Funding
P. Felix de Castro – Santander Travel Awar	£500
D. Shchukin – University of Georgia (USA) – University of Liverpool Pump-Priming Award	£2,650

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